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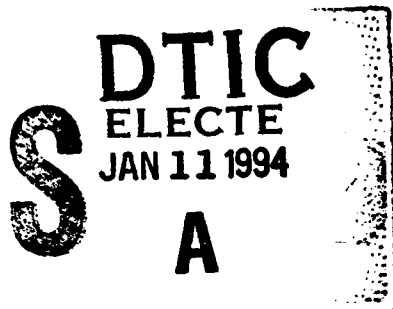
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**Observation of Crossover from Three to Two Dimensional Variable Range Hopping in
Template Synthesized Polypyrrole and Polyaniline**

by

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Observation of Crossover from Three to Two Dimensional Variable Range Hopping in Template Synthesized Polypyrrole and Polyaniline

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We report the results of a temperature dependent study of the resistance of template synthesized polyaniline and polypyrrole. Depending on the diameter of the template synthesized cylindrical fibers we observe a crossover from three to two dimensional variable range hopping. Two dimensional variable range hopping has been observed before only in ultrathin films ($< 400\text{nm}$) of amorphous silicon and germanium, but not in polymer films.

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Martin et al.¹⁻⁴ have been investigating the concept of synthesizing electronically conductive polymers within the pores of microporous host membranes. The membranes employed have cylindrical pores of uniform diameter. When a conductive polymer is synthesized in these pores, nanoscopic fibers of uniform diameter and length are obtained. This method is called "template synthesis" because the pores in the host membranes act as templates for these fibers. This method has been used to prepare nanoscopic fibers composed of polypyrrole^{1,2}, poly(N-methylpyrrole)³, poly(3-methylthiophene)¹, polyaniline³ and polyacetylene⁴. The nanoscopic conductive polymer fibers obtained show a higher degree of molecular and supermolecular order than is present in the same polymer when it is synthesized by more conventional methods^{2,3,4}. In particular, the polymer chains in these fibers are highly aligned². As a result of this enhanced order, the template-synthesized fibers have higher electronic conductivities than conventional forms of these polymers¹⁻⁴.

We have investigated the temperature dependence of conductivity in thin films composed of template-synthesized polyaniline and polypyrrole fibers. Depending on the diameter of the fibers we find a transition from 3 - dimensional (3 D) to a 2 - dimensional (2 D) variable range hopping. 2 D variable range hopping has been observed before only in ultrathin films of amorphous silicon and germanium⁵⁻⁸. In these studies the temperature dependence of the conductivity was measured as a function of the thickness of the films. At a thickness below 400 nm they found a transition from 3 D to 2 D variable range hopping indicated by a change in the exponent of the temperature dependence of the conductivity from $1/4$ to $1/3$. The crossover takes place when the hopping distance is $1/4$ of the film thickness, so that the hopping can occur only in two dimensions. We observe now for the first time a crossover from the 3 D to the 2 D variable range hopping in polymer films, and more important in films with a thickness much larger than the hopping distance. As we have pointed out before, the template method allows to produce films composed of fibers with different diameters. The diameter of the fibers influence, however, the molecular and supermolecular structural parameters^{2,3,4}. The explanation of the effect must therefore be connected with these parameters.

Nuclepore polycarbonate filters with pore diameters of 50, 100 and 400 nm were used as the template membranes^{1,2,3,4} for the synthesis. After synthesis, the template membranes were dissolved and the conductive polymer fibers were collected onto filter papers and compacted into thin films of 1.7 to 3.3 μm thickness.

Conductivity measurements were made using the four - probe method. Four gold contacts were evaporated onto the samples and connected to platinum wires (0.1 mm diameter) with silver paint. With this arrangements we have achieved contact resistances of less than 5 Ω , a value also reported by Sato et. al.⁹. Sample resistance was measured using a four wire constant voltage AC resistance bridge, which provides high sensitivity and elimination of thermal EMF errors. An thermocouple (k-typ) was used for temperature measurements from 300 K to 40 K. Below 40 K a germanium resistance was used.

Zuo et al.¹⁰ investigated the temperature dependence of conductivity in polyaniline with different doping levels and found that over the temperature range from 30 K to 280 K, independent of the doping level, conductivity varied with temperature as per equation 1.

$$\sigma = \sigma_0 \exp -(T_0 / T)^{1/2} \quad (1)$$

Unfortunately a number of models yield a temperature dependence of this type. These include three models which involve three dimensional (3 D) hopping (granular metal model^{11,12}, granular rod model¹³, 3 D variable range model with electron correlation¹⁴) and a model which involves quasi-one dimensional (1 D) variable range hopping¹⁵. Thus, the exact nature of the conduction mechanism in polyaniline remains a mystery.

Recently, Wang et al.¹⁶ reported transport and EPR studies of polyaniline which led them to conclude that there are metallic bundles in this material. However, between these bundles there are regions in which 1 D hopping dominates the macroscopic conductivity. As result, Wang et al.¹⁶ described polyaniline as a quasi 1 D conductor with 3 D "metallic" states. If the electron could hop between bundles without traversing the 1 D material, the electron motion would no longer be confined to a line and we would have 3 D variable range hopping. Mott and Kaveh^{15,23} have shown that conductivity is related to temperature in this 3 D case via:

$$\sigma = AT^{1/2} \exp -(T_0 / T)^{1/4} \quad (2)$$

where A is a constant. Such a temperature dependence of the conductivity has been reported for polypyrrole in the temperature range from about 80 K to about 10 K by Meikap et al.¹⁷ and above 100 K by Sato et al.⁹ (references therein). Recently Reghu et al.¹⁸ have observed for the first time such a temperature dependence also in some of their polyaniline samples.

If the hopping takes place in two dimensions, Mott and Davis^{5,23} have shown that the conductivity obeys

$$\sigma = AT^{-1/2} \exp -(T_0 / T)^{1/3} \quad (3)$$

As mentioned before such a temperature dependence has only been observed in ultrathin two dimensional films of amorphous semiconductors⁵⁻⁸, but never before in three dimensional polymer films.

In Figs. 1a and 2a we have plotted the resistance data of polyaniline and polypyrrole films composed of 400 nm diameter fibers as per equation 2. It can be seen that the resistance of template synthesized polyaniline and polypyrrole films composed of fibers with diameter of 400 nm shows 3 D variable range hopping in the temperature range from 160 K to 25 K and 160 K to 5 K, respectively. Again, this is only the second time that this type of temperature dependence has been observed for polyaniline¹⁸.

In Figs. 1b and 2b we show the temperature dependence of polyaniline and polypyrrole films composed of fibers with a diameter of 100 nm and 50 nm, respectively. The resistance data are plotted as per equation (3), over the temperature range from 125 K to 1.2 K and 96 K to 5 K, respectively. The data clearly obey now the 2 D variable range hopping model.

In order to find an explanation for the effect we need information about the hopping distance which is a function of T. This information can be obtained by measuring the electric field dependence of the resistance at constant temperature¹⁹⁻²¹.

For moderate fields this resistance is proportional to the $\exp -\gamma eRF / k_B T$ with $\gamma = 0.17$ for 3 D and $\gamma = 0.18$ for 2 D variable range hopping¹⁹.

As the charge of the carriers, e , the electric field, F , the Boltzmann constant, k_B , and temperature, T , are known, one can calculate the hopping distance R by determining the slope of the logarithm of the resistance versus the electric field. The absolute values of R may be doubted, because they may depend on the model used, but the relative changes should be reliable.

Fig.3a and 4a show the field dependence of the resistance for polyaniline and polypyrrole films composed of fibers with a diameter of 400 nm and Fig. 3b and 4b of polyaniline and polypyrrole films composed of fibers with a diameter of 100 nm and 50 nm, respectively, at a temperature of 4.2 K. As we did not have the possibility to use a pulse generator we could only do the measurements at this temperature, because at higher temperatures the field dependence is too small and heating effects mask the field effect. Deviations from the linear field dependence are expected¹⁹⁻²¹ and we can see from Fig. 4 that in polypyrrole the deviation from the linear behaviour occurs at fields above 20 V/cm. In case of polyaniline deviations from the linear field dependence occur at much smaller fields than in the case of polypyrrole which results in a larger error in the determination of the hopping distance. Using these data, we have determined the hopping distances at 4.2 K compiled in Table I.

We suggest an explanation for the crossover, which is based on results obtained by Lei et. al.²². They have shown using PIRAS that the conductive polymer chains are aligned perpendicular to the axis of the cylindric fiber. Their results prove that the conductive fibers have highly ordered chains on their outer surfaces but the extent of order decreases as one moves from the outer surface to the center of the fiber. Furthermore the narrowest fibers consist predominantly of the highly ordered material. If the hopping distance is larger than the thickness of the highly ordered layer the hopping within this layer will be preferred in comparison with the hopping in the direction normal to the layer. This leads to the 2 D variable range hopping in the polyaniline and polypyrrole composed of fibers with a diameter of 100 nm and 50 nm, respectively. In both films the hopping distance is larger than the layer thickness (see Table I) so that the above condition is fulfilled. This arguments are analogous to the ones used to explain the conductivity in polyaniline by Wang et al¹⁶. He concluded that despite the fact that there are metallic bundles in polyaniline, it is a quasi 1

D conductor. This is due to the fact, that between the bundles there are regions in which 1 D hopping dominates the macroscopic conductivity. In our case the hopping in the highly ordered cylindrical 2 D layers of the fibers is preferred and causes 2 D hopping to dominate the macroscopic conductivity. In the polyaniline and polypyrrole films composed of 400 nm diameter fibers, the volume ratio between the highly ordered layer and the less highly ordered regions is small. Most of the material is less ordered, which leads to an about equal hopping probability in all 3 directions and thus 3 D variable range hopping.

In summery, we have found 3 D variable range hopping in polyaniline and polyoyrrole films composed of fibers with a diameter of 400 nm. If the diameter of these fibers is reduced we find a crossover from 3 D to 2 D variable range hopping. We suggest an explanation for this crossover based on the supermolecular structure of the fibers. Work is in progress to produce 400 nm fibers, with a controlled ratio of highly ordered to less ordered material. Measurements on these materials will provide a stringent test to our explanation of the crossover. The moderate electric field dependence of resistance has been used to determine the hopping distances in these films.

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Figure Captions:

Fig. 1:

- a) Resistance versus $T^{-1/4}$ of a polyaniline film composed of 400 nm diameter fibers (Inserts: Resistance versus $T^{-1/2}$ and $T^{-1/3}$, respectively). Solid line represents the theory nearly masked by the data points.
- b) Resistance versus $T^{-1/3}$ of a polyaniline film composed of 100 nm diameter fibers (Inserts: Resistance versus $T^{-1/2}$ and $T^{-1/4}$, respectively). Solid line represents the theory nearly masked by the data points.

In a) and b) $R * T^{-1/2}$ is plotted with a logarithmic scale. The inserts allow the reader to judge the validity of the $T^{-1/2}$ and $T^{-1/3}$ fits, respectively.

Fig. 2:

- a) Resistance versus $T^{-1/4}$ of a polypyrrole film composed of 400 nm diameter fibers (Inserts: Resistance versus $T^{-1/2}$ and $T^{-1/3}$, respectively).
- b) Resistance versus $T^{-1/3}$ of a polypyrrole film composed of 50 nm diameter fibers (Inserts: Resistance versus $T^{-1/2}$ and $T^{-1/4}$, respectively).

(Comments concerning the inserts see Fig. 1)

Fig. 3: DC Field dependence of the resistance of a polyaniline film

- a) composed of 400 nm diameter fibers
- b) composed of 100 nm diameter fibers

Fig. 4: DC Field dependence of the resistance of a polypyrrole film

a) composed of 400 nm diameter fibers

b) composed of 50 nm diameter fibers

Table Caption:

Material	Fiber diameter [nm]	Hopping Distance [nm]
polyaniline	400	500±50
polyaniline	100	402±50
polypyrrole	400	140±7
polypyrrole	50	100±5

Table I: Hopping distance at 4.2 K for polyaniline and polypyrrole films composed of fibers with different diameters

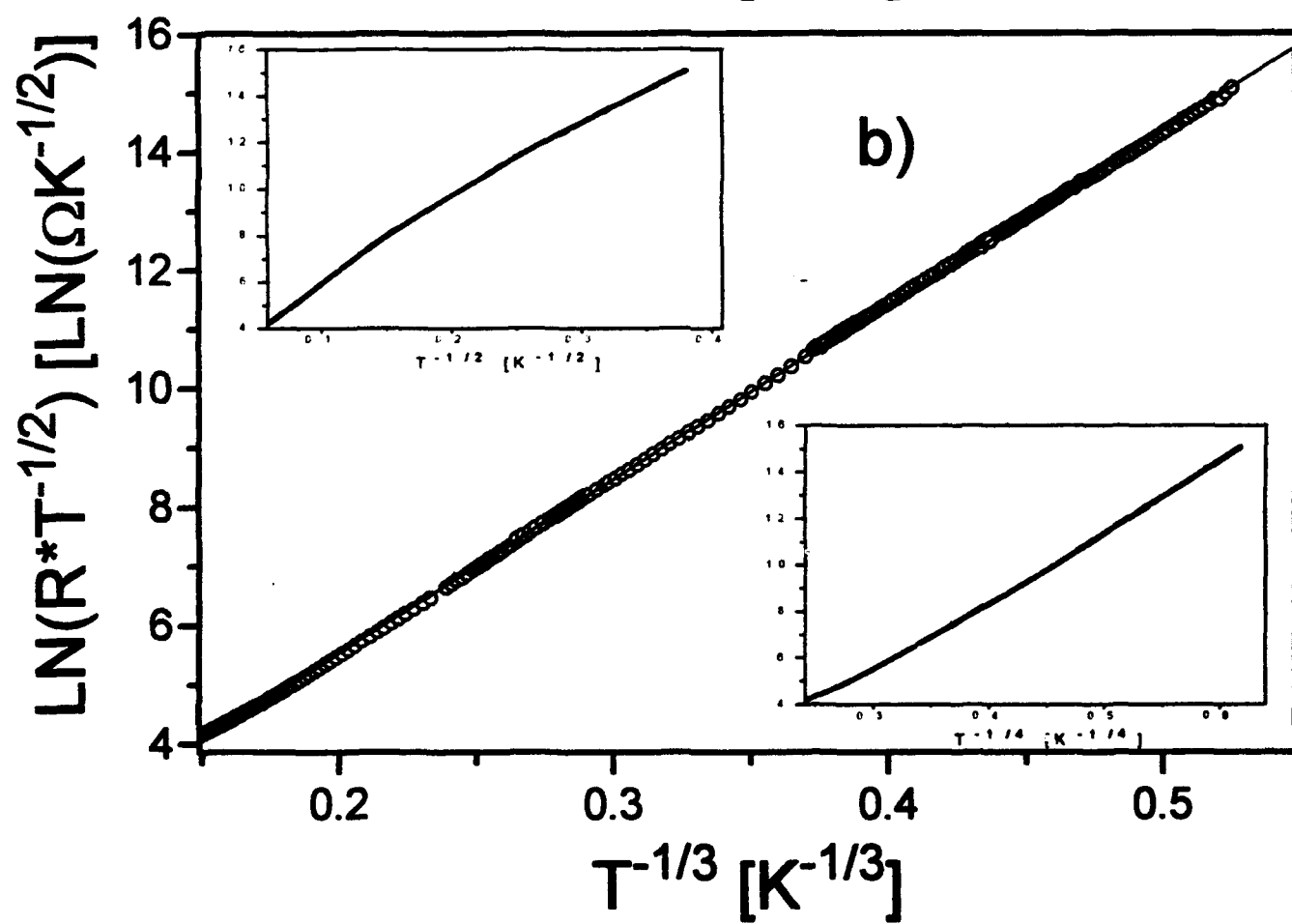
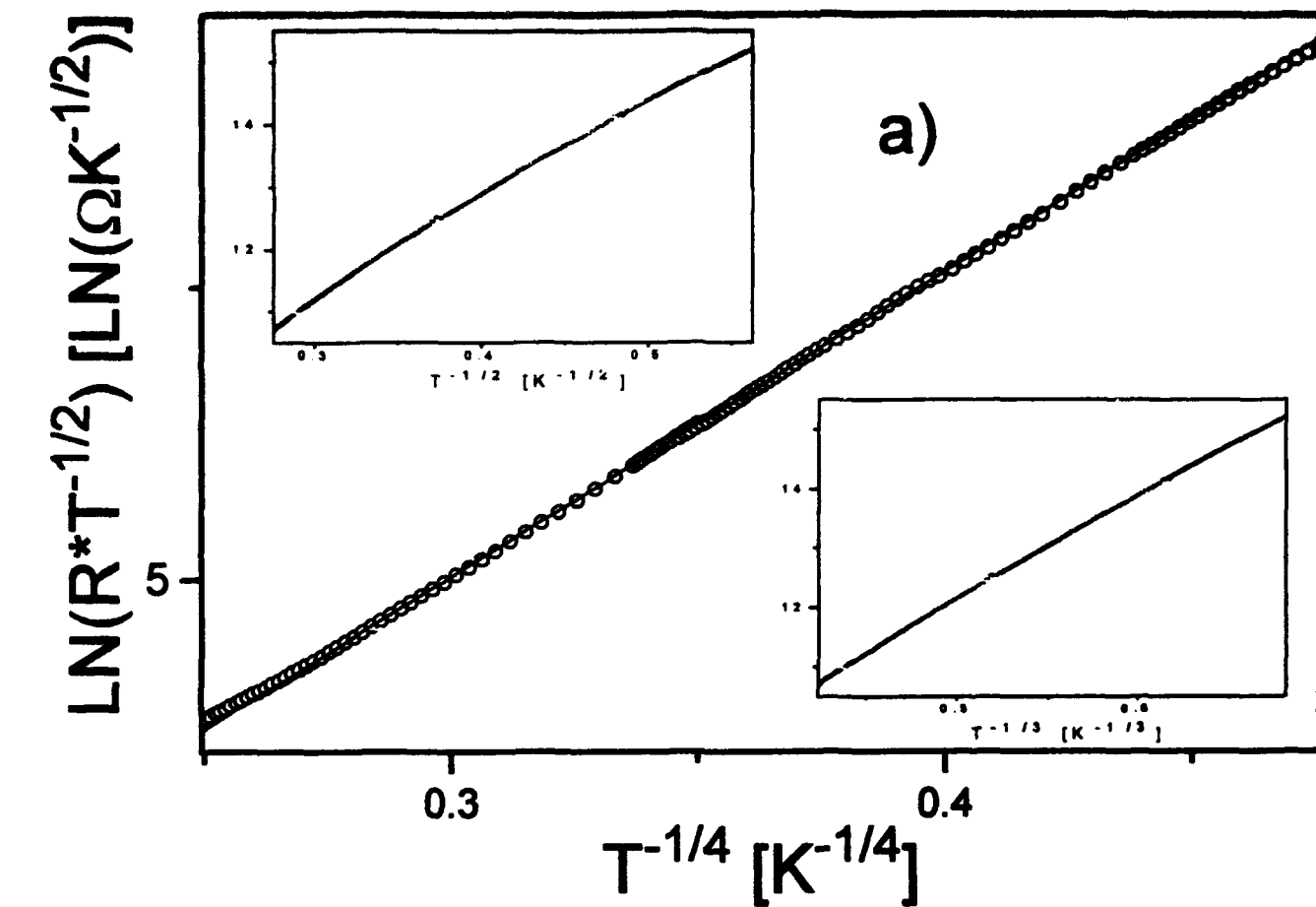


Figure 1

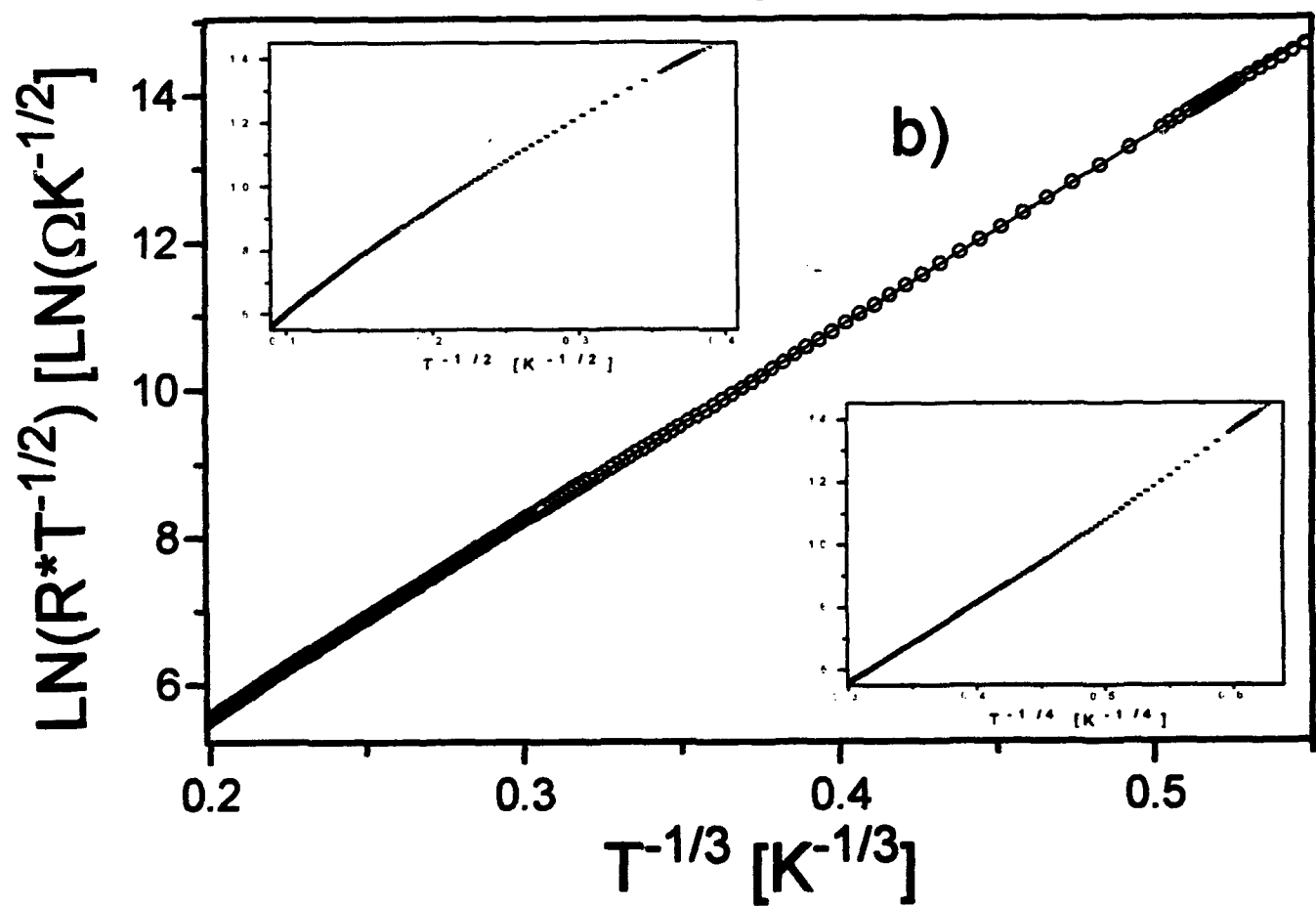
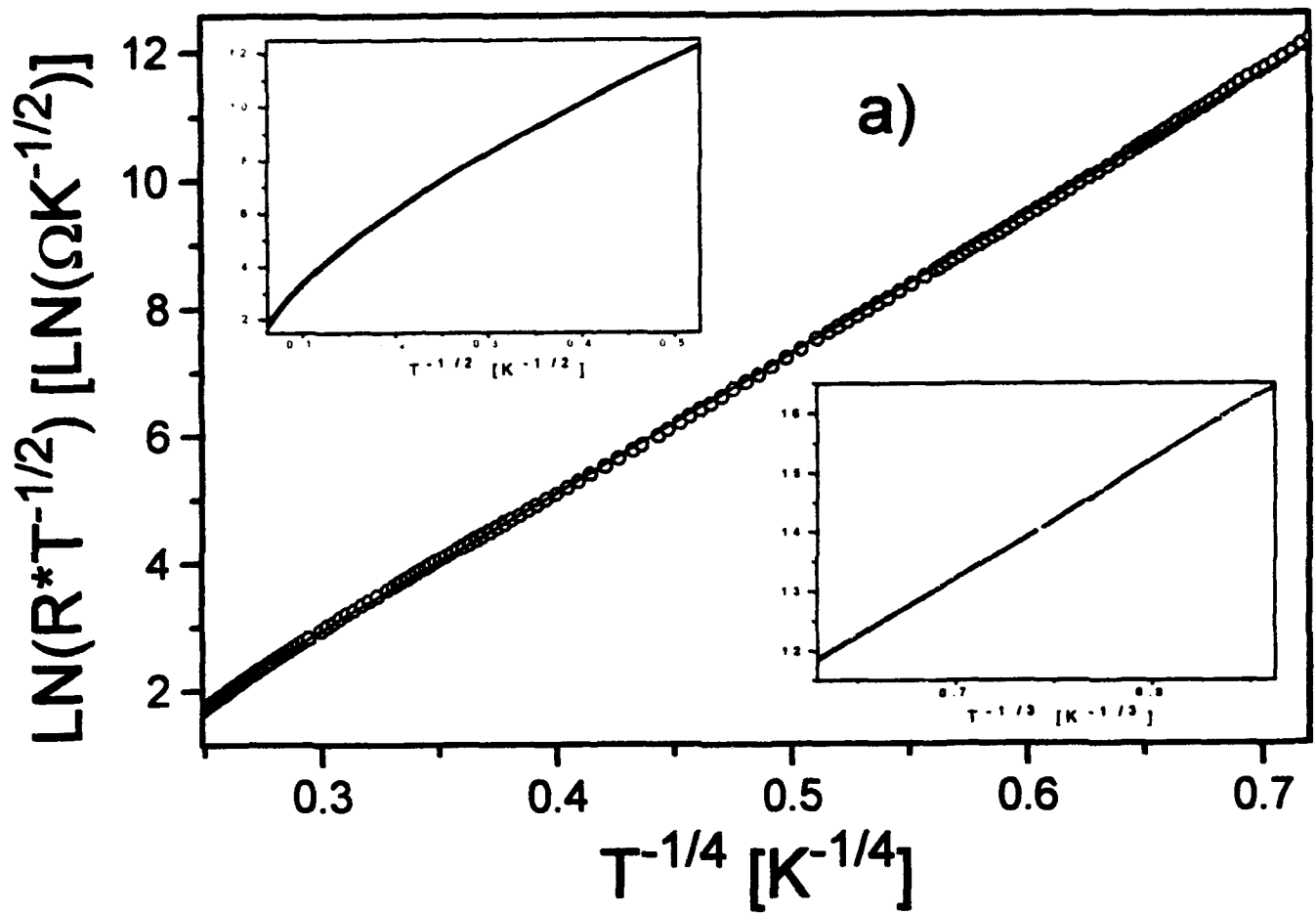


Figure 2

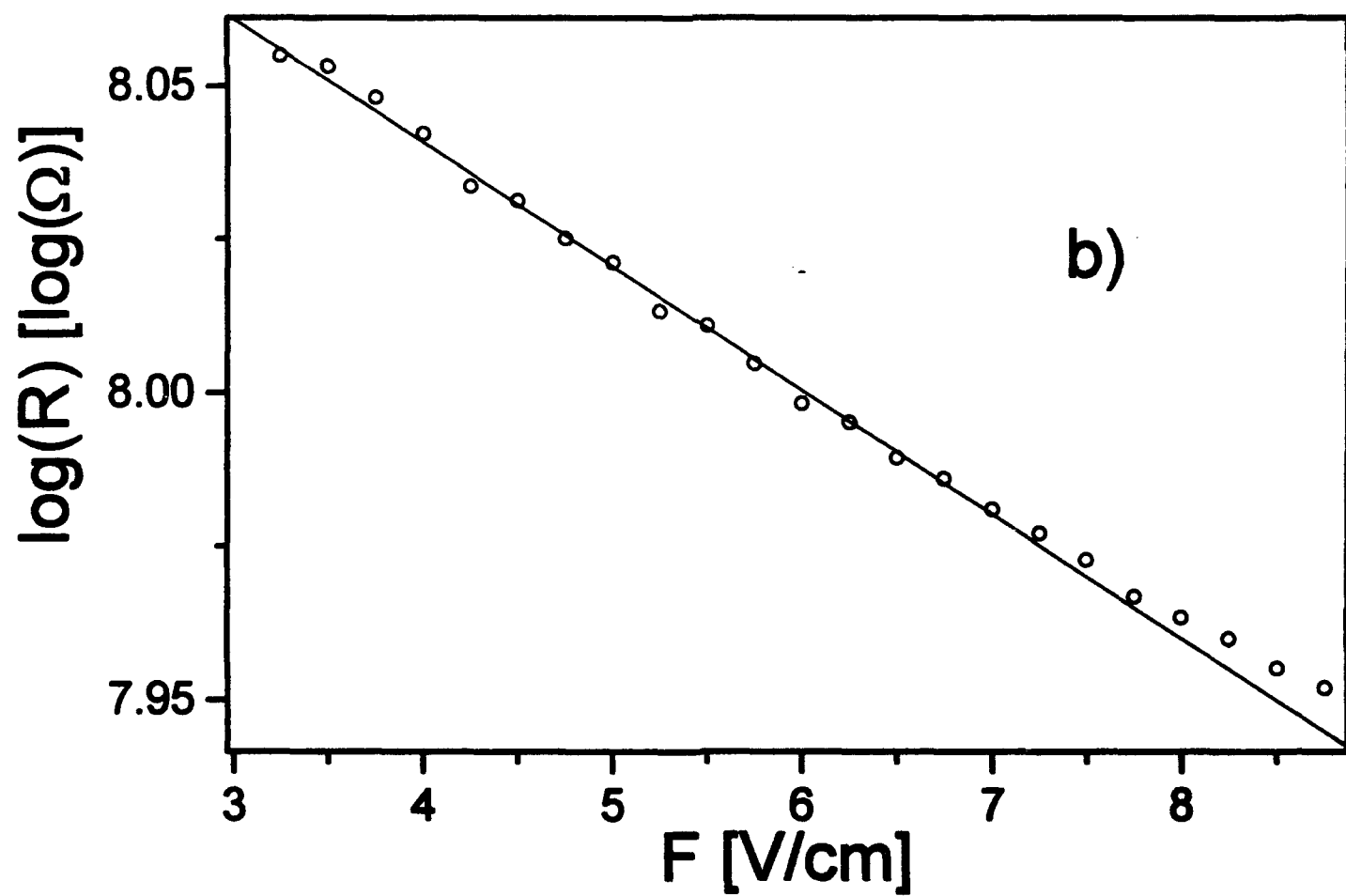
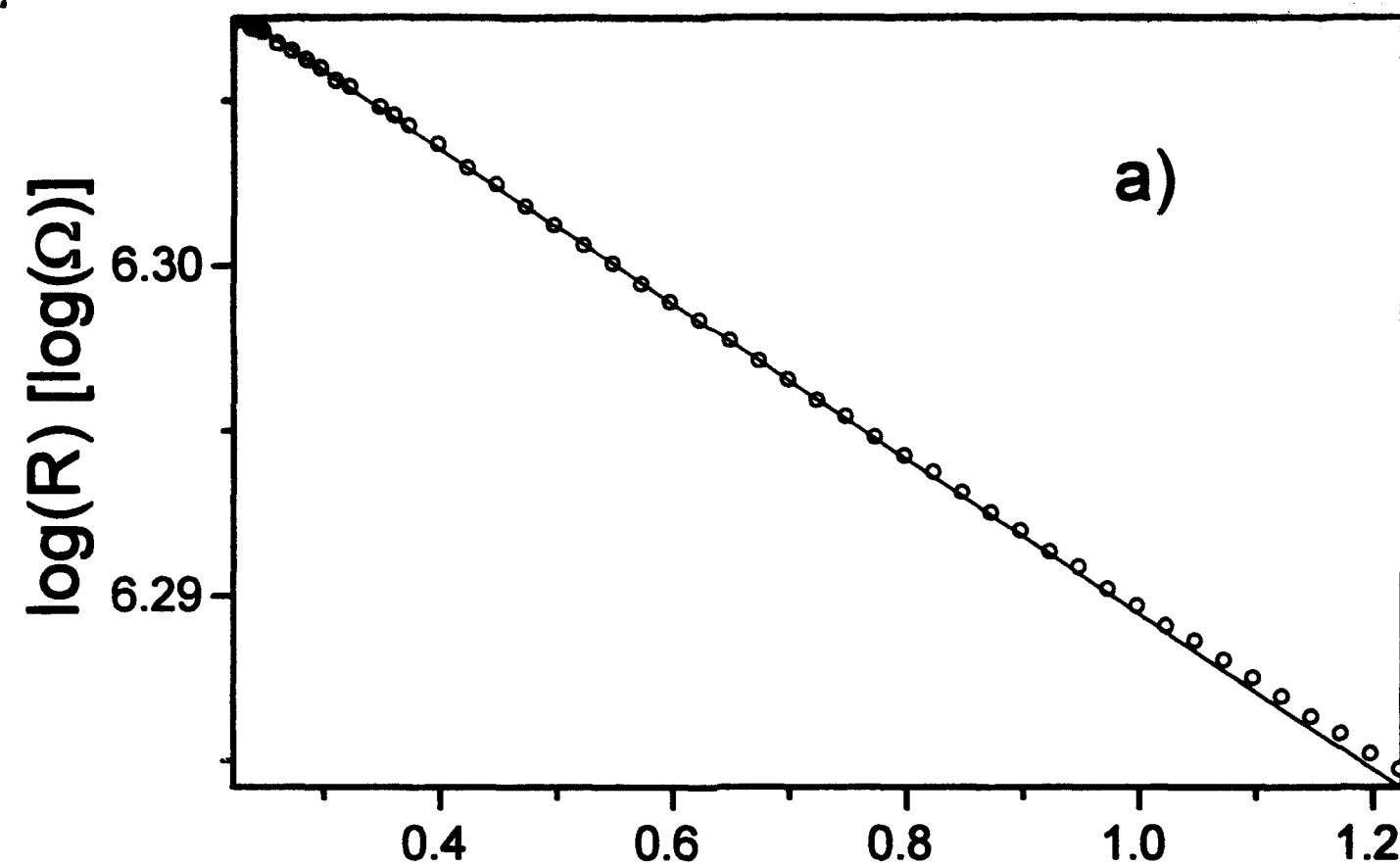


Figure 3

